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CLAY-SILICON CARBIDE REFRACTORIES BASED ON TECHNOGENIC MATERIALS PRODUCED BY SLIP CASTING

V. P. Sivov[1]

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The results of studying the variations in the main physicotechnical properties of clay-silicon carbide refractories, which are produced on the basis of broken silicon carbide plates by the slip casting method, after multiple heating and chilling are considered. The resulting refractories are recommended for use as refractory stacks and saggers in the production of fine ceramics.

Various types of refractories are used in fine ceramics production for refractory stacks and saggers. The refractories based on silicon carbide have recently become quite common at Ghzel' ceramic factories. Silicon carbide refractories based on a refractory clay binder are used up to the temperature 1380 – 1410°C. This material is 2.5 – 3 times stronger than the clay-chamotte refractory, which makes it possible to produce articles with thinner walls and increase the furnace efficiency. The high thermal conductivity of the silicon carbide refractory (8 times higher than that of clay-chamotte material) provides for shortening the duration of heating and chilling of fired articles and improving their quality [1].

Refractories made on the basis of SiC (70 – 80%) with a clay binder and an alumina additive have the following basic parameters [2]: average apparent density 2.4 g/cm^3, open porosity 14 – 22%, bending strength 10 MPa, TCLE 5.5×10^{-6} K^{-1}, and service temperature 1400°C. The main defect of silicon carbide is its tendency for volume increase when the service temperature exceeds 1000°C, especially in the presence of water vapor, which is always present in furnace gases. After engobing, the oxidation of refractory articles decreases.

The refractory mixtures are prepared by three methods: wet, slip casting, and dry. The slip method for producing saggers in gypsum molds does not require bulky press machinery and complicated molds, which relatively soon wear under the effect of the molding mixture components (silicon carbide and corundum). The slip casting method is used for making shaped and thin-walled saggers of mixtures with a high degree of grog addition, which is essential in making articles of complex shapes.

The implementation of the slip casting method in sagger production allows for obtaining silicon carbide saggers with a long service life and of virtually any size, which is very significant in the production of small-scale or unique articles. However, due to the high cost of silicon carbide (8000 – 10,000 rubles per ton), the application of such saggers at porcelain factories in the Gzhel' region is limited.

In recent years the Gzhel'skii Art Design College and Gzhel' Company have studied the technology of producing silicon carbide saggers on a clay binder by slip casting in gypsum molds, using either silicon carbide grinding powder or waste generated by silicon carbide products (plates, saggers) after their multiple use in firing porcelain articles [3, 4]. The research established the possibility of using silicon carbide plate scrap in the composition of slip mixtures for sagger production.

The use of waste generated by ceramic works in making heat-resistant refractories makes it possible to solve the problem of the utilization of broken plates and saggers and to a great extent decrease the production cost of the refractories via a complete replacement of expensive silicon carbide.

The results of studying the physicomechanical properties of various mixtures are given in Table 1 [4]. As can be seen, samples based on broken carborundum plates in their main parameters surpass the analogous parameters of the reference mixture based on SiC grinding powder.

The silicon carbide contained in the form of grains in broken silicon carbide plates has decreased oxidizability, which increases the mechanical strength of the material due to the existence of active cristobalite and mullite films on the grain surface, which activates the formation of mullite in firing of the refractory.

The industrial testing of the optimum mixture composition based on silicon-carbide plate waste at the Gzhel' Company demonstrated that using broken silicon-carbide plates in producing finely dispersed heat-resistant refractories in-

[1] Gzhel'skii Art Design College, Vladimir Region, Russia.

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stead of expensive SiC grinding powder makes it is possible to:

– reduce more than 2.5 times the cost of refractory production;

– utilize waste of carborundum plates and saggers generated at the factory;

– free production space intended for this waste storage.

The purpose of the present study was to investigate the modification of the properties of the clay-silicon carbide refractories based on industrial waste (broken silicon carbide plates and saggers) after multiple heating and chilling.

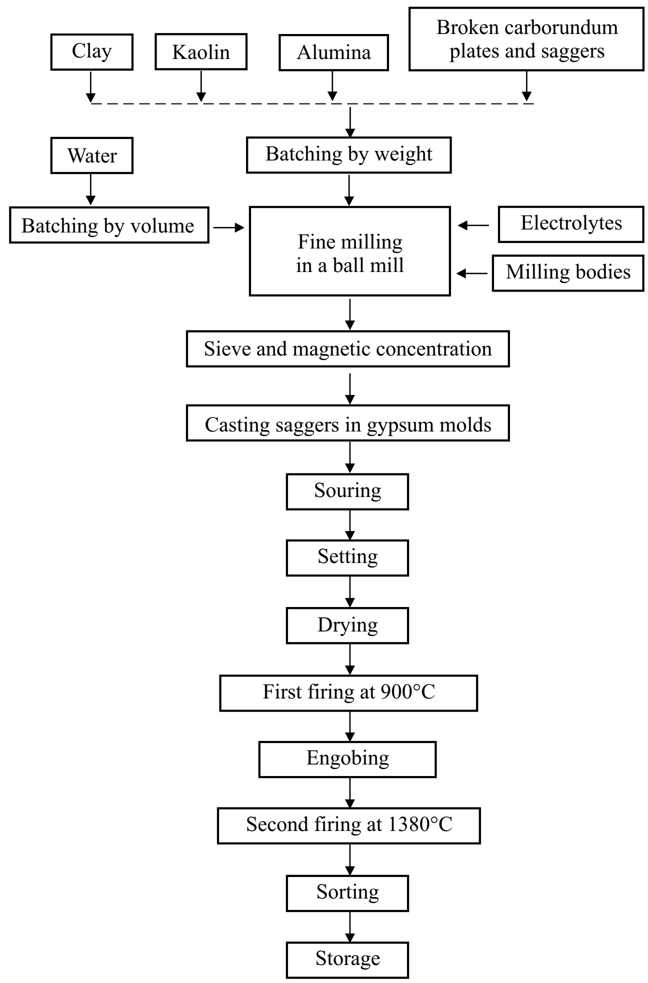
The initial mixture selected for investigation was mixture M3 tested earlier in industrial conditions at the Gzhel' Company. The mixture had the following composition (here and elsewhere wt.%): 20 Latnenskoe clay, 10 Prosyanovskoe kaolin KPF-2, 10 alumina, 60 broken carborundum plates and saggers. Electrolytes were introduced in the mixture above 100%: liquid glass (0.6%), soda ash (0.2%), and sodium pyrophosphate (0.1%).

The chemical composition of the industrial waste (broken silicon carbide plates and saggers) is as follows (%): 73.48 SiC, 23.16 SiO_2, 1.69 Al_2O_3, traces of Fe_2O_3, 0.36 CaO, 0.26 MgO, 0.17 K_2O, 0.19 Na_2O, traces of TiO_2, traces of SO_3. The chemical composition of the industrial waste shows a sufficiently high content of SiC, since in spite of multiple firing of plates and saggers, SiC grains enter in chemical reactions only at a small depth from the surface (up to 10 – 12 μm).

The slip mixture was prepared by joint milling of the components in a ball mill to a residue of 8 – 10% on a No. 0063 sieve. The slip moisture was maintained constant at 32%. The rheological parameters of the slip are: density 1.79 g/cm^3, fluidity 4 sec, thickening coefficient 1.25.

The process of producing silicon-carbide saggers based on broken carborundum plates and saggers was carried out according to the technology adopted at the Gzhel' Company (Scheme 1).

Scheme 1



To study the modification in the properties of clay-silicon carbide refractories after multiple heating (maximum temperature 1380°C) and chilling, a lot of 40 oval and round-shaped saggers was manufactured.

The modifications in the physico-mechanical properties of saggers were monitored after 1, 5, 9, 12, 24, 36, and 60 cycles. For this purpose after each control heating – chilling cycle the state of the saggers was visually inspected; their volume weight, water absorption, bending strength, and TCLE were determined, and the microsctructural and x-ray quantitative phase analysis was performed. To compare the changes in the phase (material) composition, the following samples were taken: a waste silicon carbide plate, a sagger after 1 firing cycle, and a sagger after 60 firing cycles. These investigations were completed after the saggers were subjected to 60 heating – chilling cycles.

Visual inspection of saggers after the successive control cycle did not reveal any defects, such as deformations, cracks, chips, etc.

The results of determining the density and water absorption are shown in Table 2.

TABLE 1

Parameter	Initial mixtures based on SiC grinding powder	Mixtures based on broken silicon carbide plates		
		M1	M2	M3
Static bending strength, MPa	40.0	40.4	49.0	53.0
Water absorption, %	18.0	15.5	16.4	17.7
Overall shrinkage, %	5.3	5.8	5.1	3.8
Porosity, %	20.0	18.8	21.0	19.5
TCLE in temperature interval 50 – 600°C, 10^{-6} K^{-1}	4.58 – 5.00	6.1 – 7.2	6.2 – 7.4	6.3 – 7.7
Volume weight, g/cm^3	1.8	1.74	1.76	1.78
Heat resistance of sample after 10 thermal cycles (bending strength), MPa	38	32	36.9	41.1

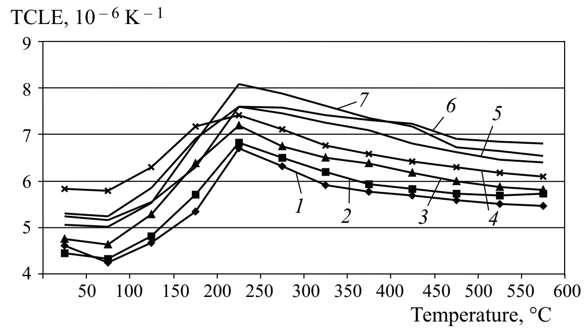


Fig. 1. Variations in TCLE of saggers depending on the number of heating – chilling cycles: *1*, *2*, *3*, *4*, *5*, *6*, and *7*) 1, 5, 9, 12, 24, 36, and 60 cycles, respectively.

The analysis of the obtained data indicates that as the number of heating – chilling cycles increases (from 1 to 24), the sagger density grows from 1.82 to 1.90 g/cm^3, and on further increase in the number of cycles (from 24 to 60) it decreases from 1.90 to 1.82 g/cm^3.

As the number of heating – chilling cycles increases, the water absorption of the samples (beams 100 × 10 mm) cut out of the sagger gradually decreases from 21.4% after 1 cycle to 15.7% after 60 cycles.

TABLE 2

Number of heating – chilling cycles	Mean density of sagger, g/cm^3	Water consumption of sagger, %
1	1.82	21.4
5	1.86	20.5
9	1.89	20.2
12	1.89	20.0
24	1.90	18.3
36	1.83	16.5
60	1.82	15.7

The results of the modifications in the bending strength of samples cut out of the sagger are indicated below:

Number of heating – chilling cycles	**Bending strength of saggers, MPa**
1	37.2
1	37.2
5	32.4
9	33.3
12	29.5
24	32.7
36	35.0
60	39.1

As the number of cycles grows from 1 to 12, a certain decrease in the bending strength of the articles is registered (from 37.2 to 29.5 MPa). From 12 to 60 cycles the strength of the samples gradually grows (from 29.5 to 39.1 MPa). This is related to the fact that a certain degree of SiC oxidation occurs during the first 12 cycles, which is accompanied by loosening of the structure, whereas intense mullitizing of the articles is registered from cycle 12 to cycle 60, which increases their mechanical strength.

The results of determining the TCLE on a BHR-802 dilatometer are given in Fig. 1. It can be seen that as the number of heating – chilling cycles grows, the TCLE slightly increases. A sharp increase in the TCLE in seen in the temperature interval 180 – 270°C in all testing cycles, which is accounted for by the transformation of β-cristobalite into α-cristobalite and is accompanied by a change in the sample volume.

The results of the microstructural analysis of the sample cut out of the sagger after a certain number of heating – chilling cycles are shown in Table 3.

The study of the microstructure of the sample after multiple heating and chilling demonstrated more clearly expressed mullitizing. As the number of heating – chilling cycles in-

TABLE 3

Parameter	Microstructure of samples after heating – chilling cycles						
	1	5	9	12	24	36	60
Porosity, %	19.7	19.2	18.9	18.9	18.8	18.0	17.0
Pore size, μm:							
average	16.4	12.9	12.9	12.9	14.8	14.6	15.3
maximum	160	160	165	165	170	180	180
Silicon carbide content, %	36.0	36.6	34.1	34.1	31.8	30.2	25.7
Silicon carbide grain size, μm:							
average	21.0	22.5	21.0	21.0	23.3	23.7	25.0
maximum	160	165	165	170	170	170	160
Alumina content, %	3.2	3.3	3.4	3.5	3.3	3.1	2.6
Alumina grain size, μm:							
average	15.0	13.0	12.0	10.0	10.8	8.0	10.6
maximum	85	90	95	100	100	100	100
Corundum content, %	9.2	9.0	8.8	8.6	8.3	8.0	7.8
Corundum grain size, μm:							
average	22.6	22.4	21.9	21.5	20.0	19.5	19.1
maximum	70	70	65	60	60	60	60

TABLE 4

Material	Weight content, %						
	α-SiC	mullite	cristobalite	tridimite	vitreous phase	quartz	corundum
Broken silicon carbide plates	41.0	7.0	16.0	26.0	6.0	2.5	1.5
Silicon carbide sagger after heating – chilling:							
1 cycle	39.0	27.0	18.0	6.5	3.0	1.0	5.5
60 cycles	35.0	32.0	18.0	6.5	3.0	2.5	3.0

creases, the crystallization of the glass ceramic binder becomes more homogeneous. Mullite is encountered both in the form of clusters and in the form of a glass ceramic material with needle size ranging from 2 – 5 to 10 – 12 μm. After 9 heating – chilling cycles, a clearly defined fused edge 1 μm thick is visible in silicon carbide saggers based on the plate waste, and as the number of cycles increases, the edge thickness grows to 2 μm and more. The structure of the material is heterogeneous, the shape of SiC grains is fragmental, and the pore shape is irregular, isometric, and elongated.

Researchers at the N. M. Fedorovskii All-Russian Research Institute for Mineral Materials (VIMS)[2] investigated the phase composition of the sample of silicon carbide sagger based on industrial waste, namely, broken silicon carbide plates. The results of the x-ray quantitative phase analysis are indicated in Table 4.

As the number of heating – chilling cycles increases, the content of α-SiC in the saggers decreases from 39 to 35%, which is determined by the oxidation of silicon carbide due to the oxygen contained in the fuel combustion products. At the same time, the amount of mullite crystals $3Al_2O_3 \cdot 2SiO_2$ grows from 27 to 32%, and the content of cristobalite and tridimite remains constant and constitutes, respectively, 18.0 and 6.5%. As the number of heating – chilling cycles grows from 1 to 60, the quantity of the vitreous phase in the sagger remains constant and is equal to 3%.

The content of free silica grows from 1 to 2.5%, which is evidence of SiC oxidation according to the reaction

$$SiC + 2O_2 = SiO_2 + CO_2$$

with the formation of free silicon dioxide.

[2] The material was analyzed on a DRON-3 x-ray diffractometer by G. K. Krivokoneva, a Leading Researcher at VIMS, Candidate of Geol-Mineral. Science.

The amount of corundum decreases from 5.5 to 3.0%, which is related to its chemical reaction with silicon dioxide and the formation of mullite according to the reaction

$$3Al_2O_3 + 2SiO_2 = 3Al_2O_3 \cdot 2SiO_2.$$

The broken silicon carbide plates used to produce finely disperse silicon carbide refractories have a high content of α-SiC (up to 41%) and up to 7% mullite, which leads to increased mechanical strength and activates the formation of mullite in the resulting material.

Cristobalite, which is contained in broken silicon carbide plates in the amount of 18%, has a significant effect on the TCLE of the mixtures based on plate waste, especially in the temperature interval 180 – 270°C, as the result of the volume expansion of the material. This should be taken into account in selecting the temperature curve for firing the refractories in the furnace, i.e., the process of heating articles within the specified temperature interval should be retarded.

Thus, silicon carbide refractories made by slip casting using broken silicon carbide plates are recommended for application as refractory stakes and saggers in the production of fine ceramics.

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